Analytical Chemistry: Absorption and Emission Spectroscopy

CHEM 10

Mr. Brakke

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Color of Compounds and Solutions

- Please visit my class wiki
  - Martinbrakkeibchem.escuelacampoalegre.wikispaces.net/SAAS+Day
  - Complete the Pre-Assessment Survey
  - Take out a piece of scratch paper, fold in a triangle and clearly write your first name on it.
- Questions of the day:
  - Hoe can an element be identified by its emission spectrum?
  - How does emission differ from absorption?
  - How are emission spectra identified as either a qualitative or a quantitative collection of data.
  - What elements are considered to be transition metals?
  - Why do transition metals appear colored when dissolved in solvents?
  - List a few factors that could change the solutions of the same transition metal to result in different color solutions.
  - What do decomposition reactions require?
  - How can the same transition metal make two different colored solutions?
  - List relative ligand field splitting of several colored compound solutions

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Wave Properties

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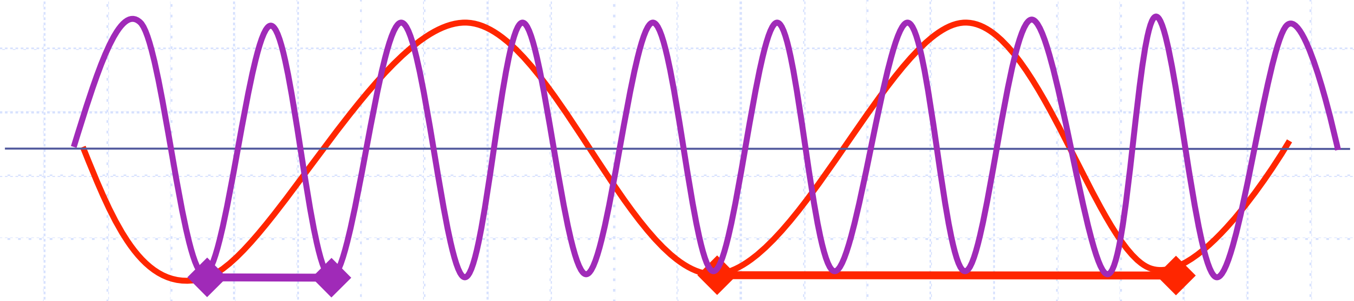
From Atomic Structure

- In a vacuum all electromagnetic waves travel at the same speed (c), $c = 3x10^8$ m s^{-1}
- **Wavelength** (lambda, λ) is the distance between two neighboring crests or troughs of a wave
- **Frequency** (f) is the number of waves that pass a given point in one second, recorded in **hertz** (Hz)
- **Speed** (c) is the distance travelled by a wave in one second, recorded in meters/second (ms^{-1})
- **Wave Equation** expresses the relationship between each of the three, where c (speed) is the speed of light, $c = 3 \times 10^8$ ms^{-1}.
  - **$C = f\lambda$ or $f = c / \lambda$**



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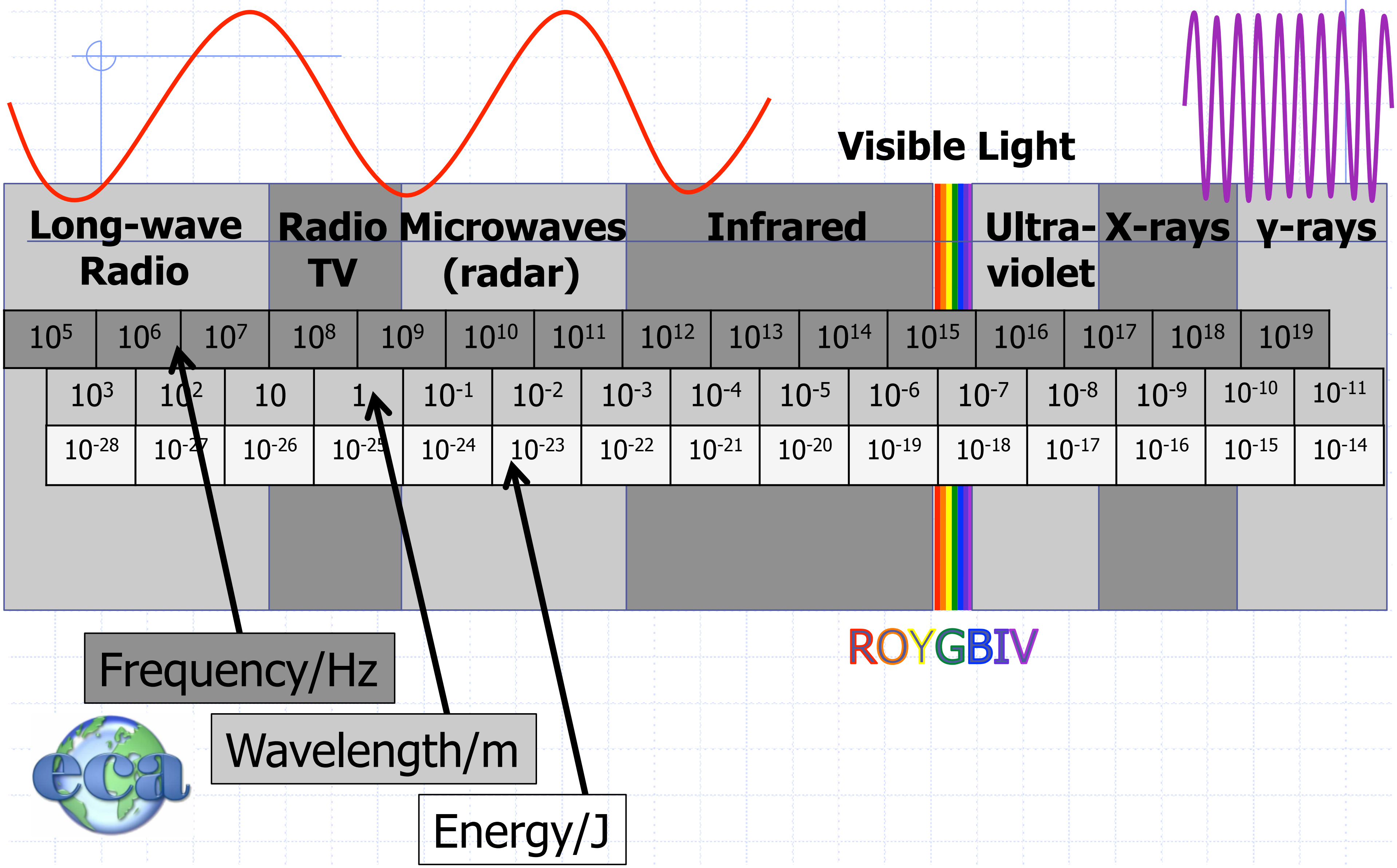
Electromagnetic Spectrum



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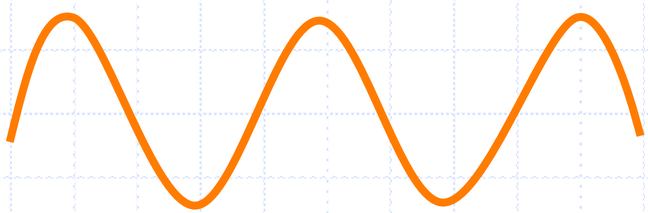
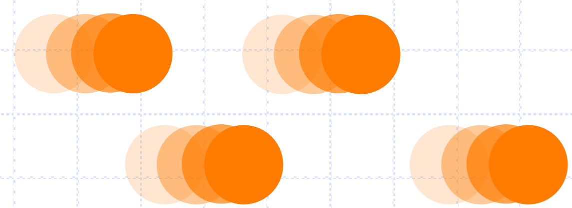
Planck’s constant

From Atomic Structure

- Light can also be described as particles (photons) which are tiny packets of energy
- The wave and particle models can be related through **Planck’s constant**.
  - **$E = hf$**
  - E is the energy of a photon (in joules)
  - h is Planck’s constant (6.63×10^{-34} Js)
  - f is the frequency as before





- A Photon of high frequency electromagnetic radiation has more energy than one of low frequency.

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What we see:

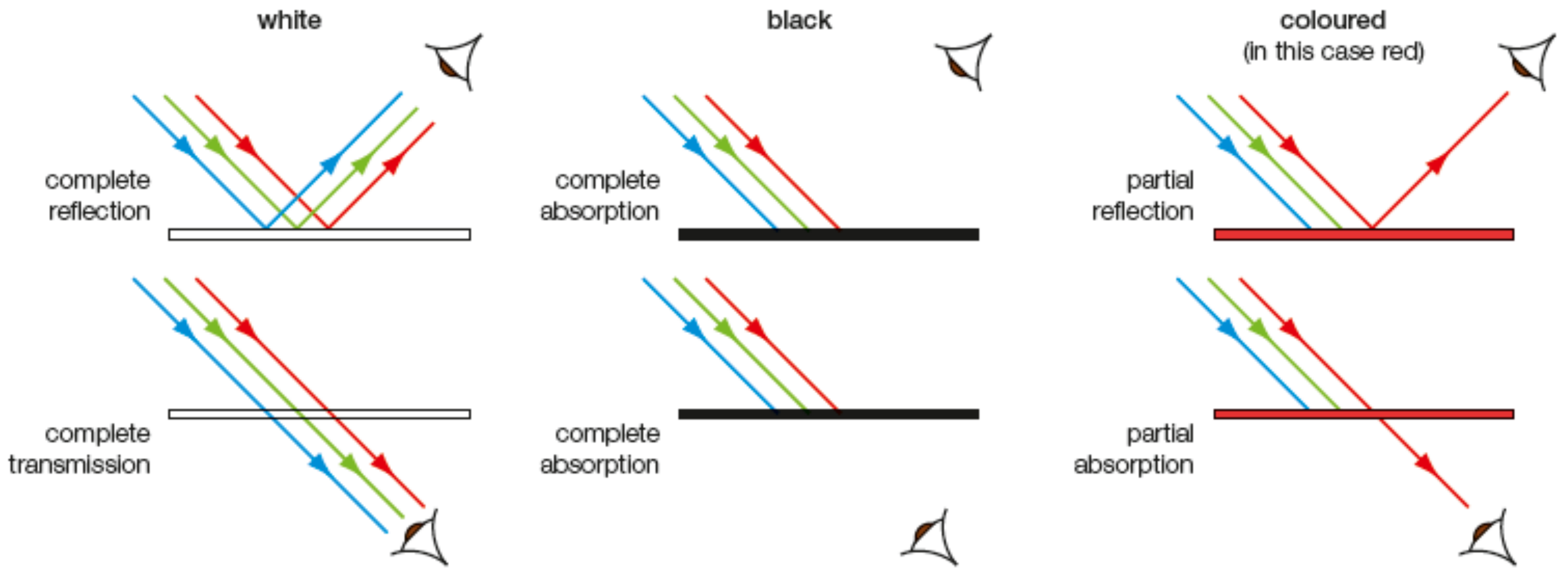

Figure 21.89 Colour and absorption of visible light wavelengths

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Complementary Colors

What would be seen if:
- All colors are present?
- No colors present?

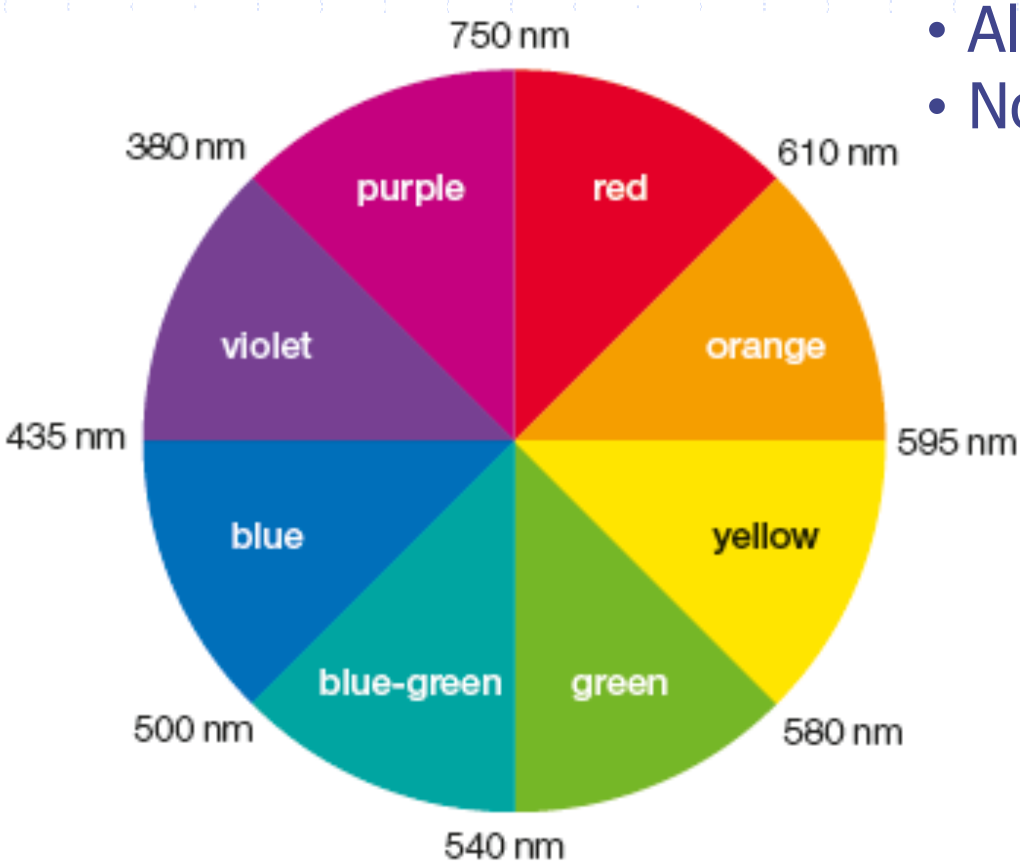

Figure 21.90 A simple colour wheel: complementary colours are opposite one another

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Absorption of Light

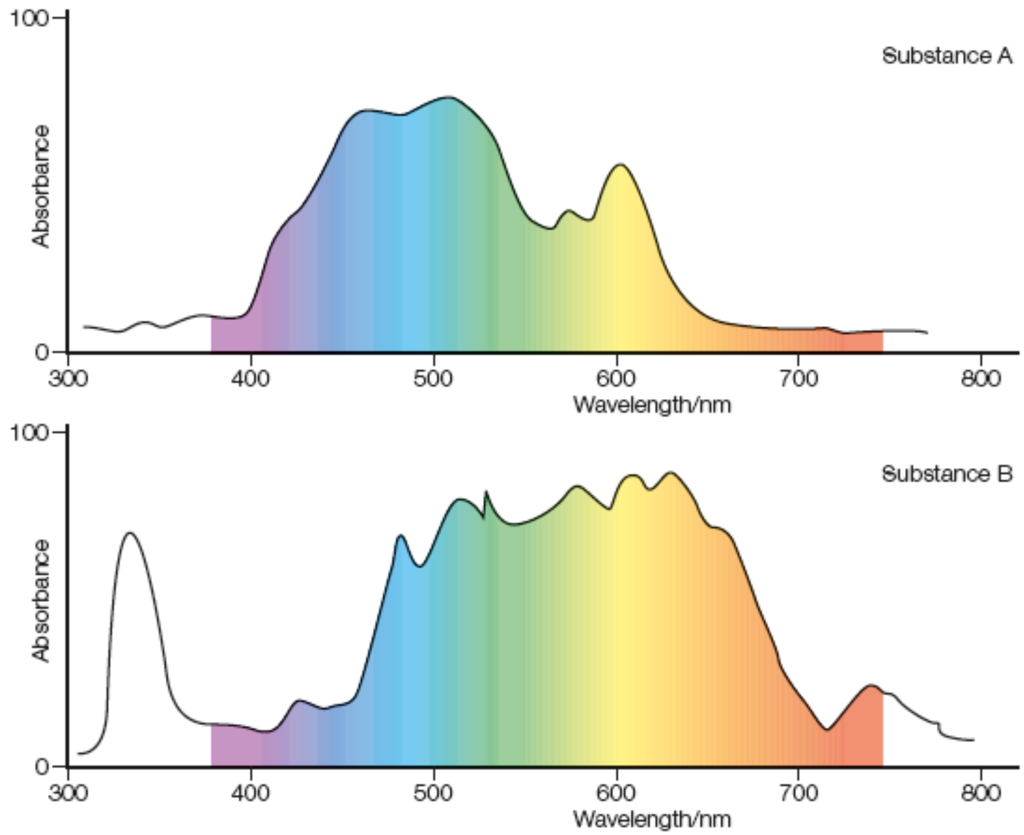

Figure 21.91 Absorption spectra for substances A and B

In this visible absorbance spectra, what color would be seen by the naked eye?

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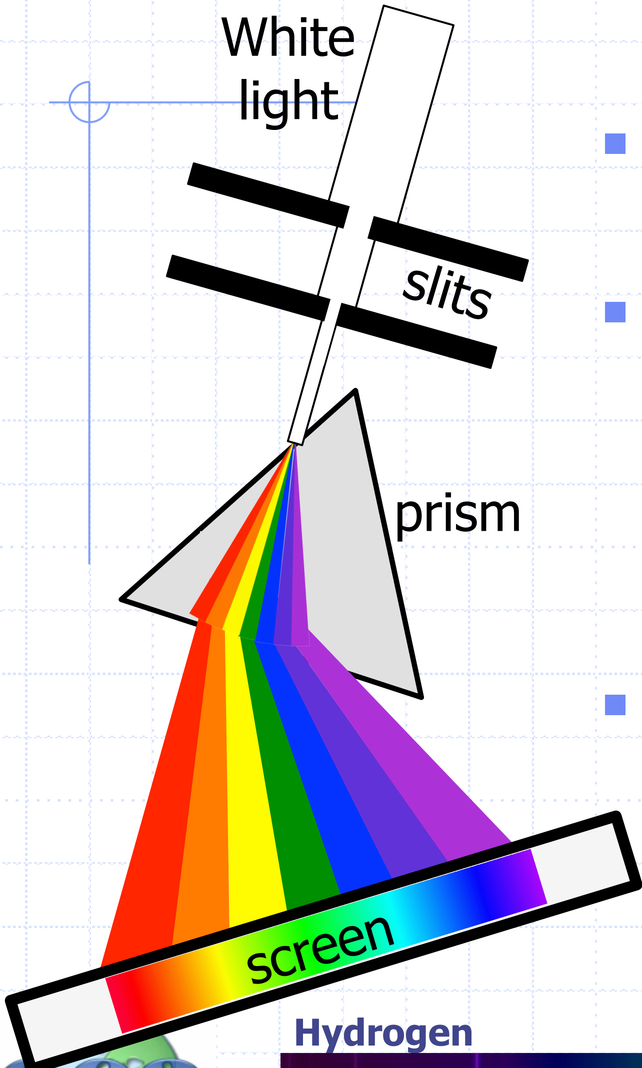
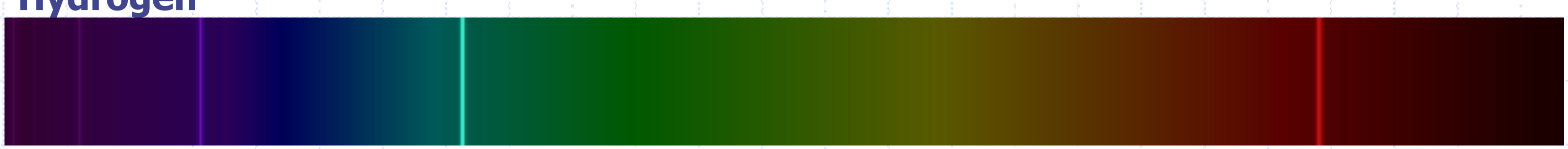
Visible Spectrum (continuous vs line)

From Atomic Structure



- **White light** is an intense blend of all colors of light
- A **continuous spectrum** of light is composed of all the visible colors of white light. Like a rainbow where there is a smooth blend of an infinite number of colors
- A **line spectrum** is one which contains only a narrow emission of colors on a black background

Hydrogen



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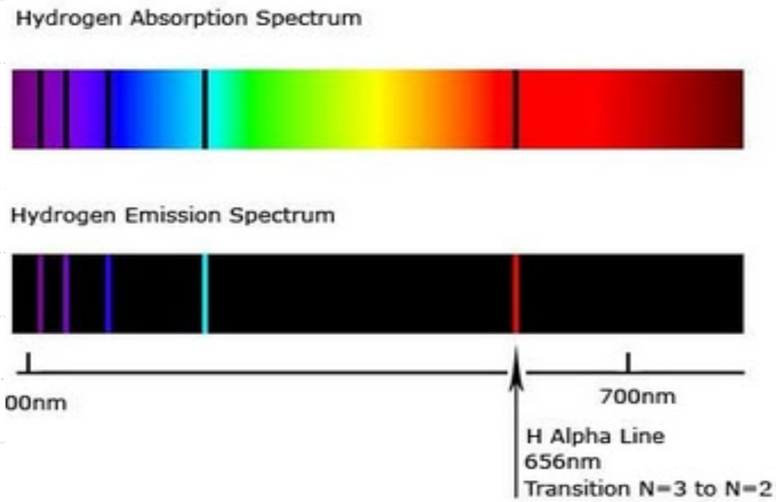
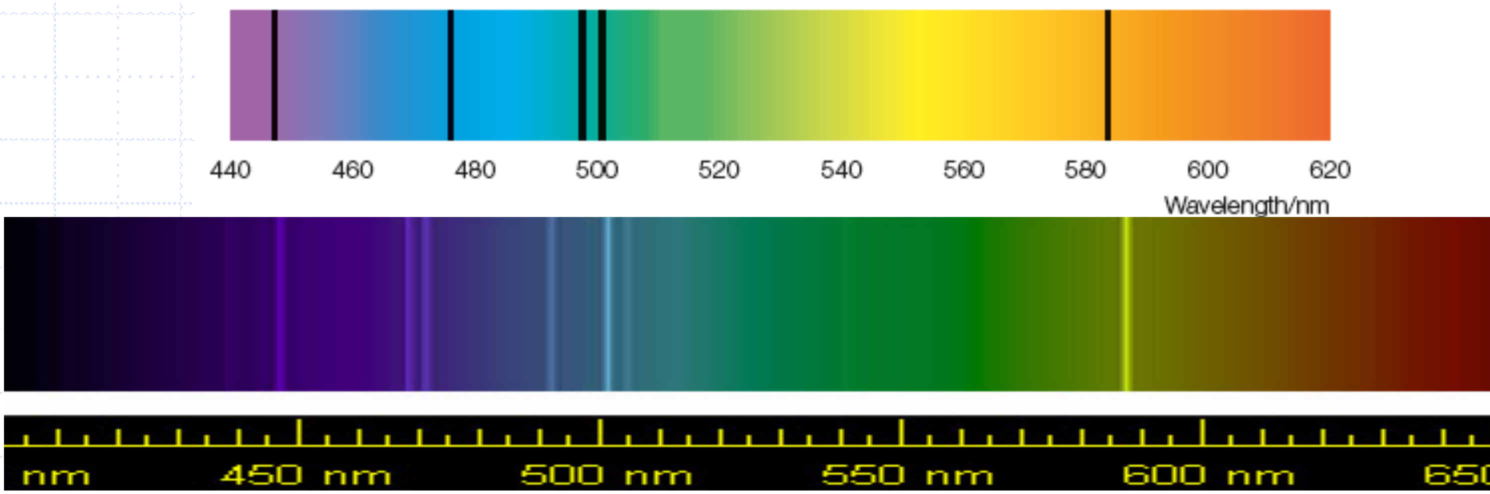
Atomic Absorption vs Emission

Hydrogen: Absorption (top) and Emission (bottom)



The absorption and emission spectrums are equal and opposite of each other

Helium: Absorption (top) and Emission (bottom)



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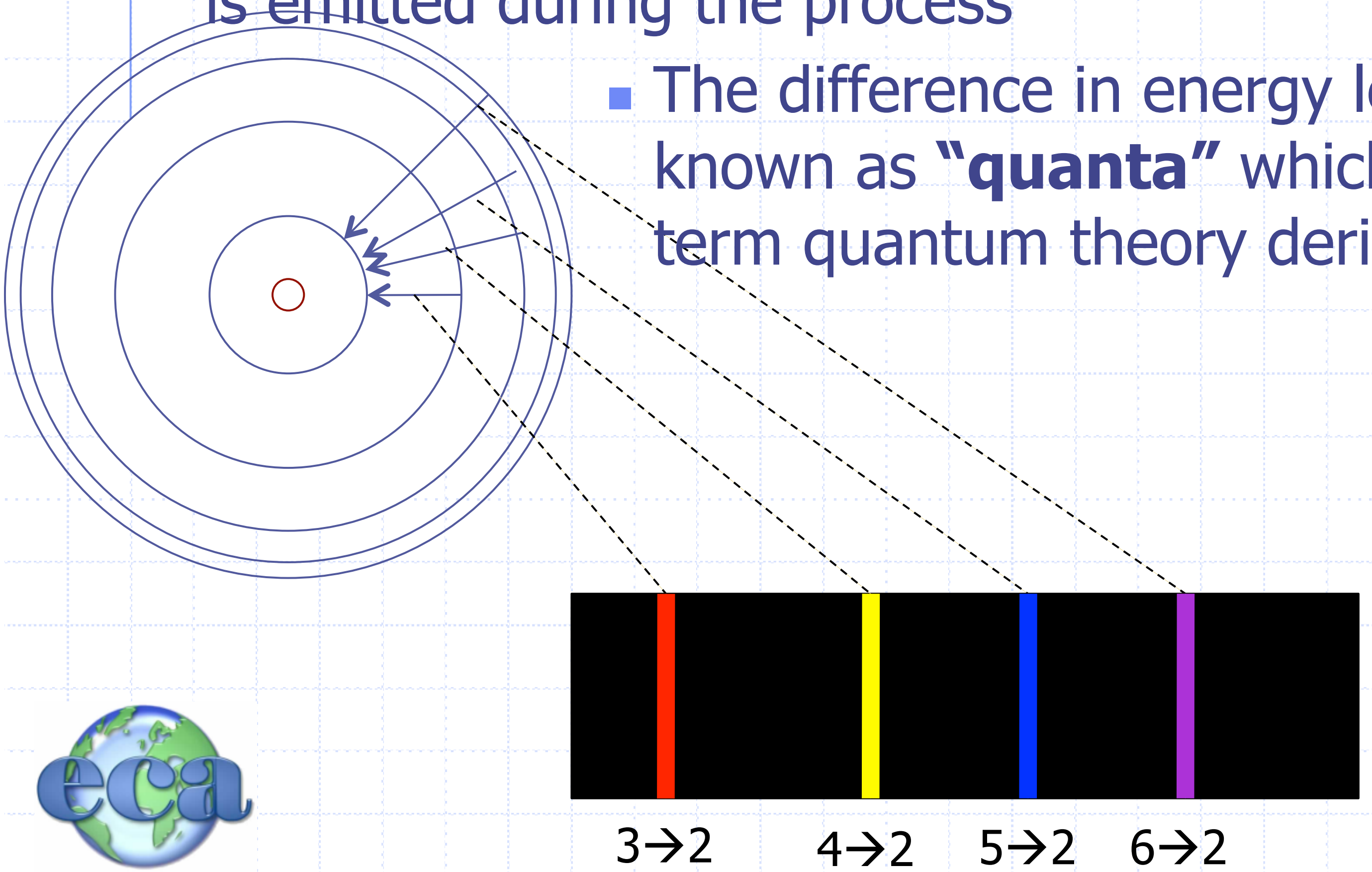
Electron Emission Energy

- The difference in energy levels as electrons move corresponds to the energy of the wavelength of light that is emitted during the process
  - The difference in energy level is also known as **"quanta"** which is where the term quantum theory derives itself



**This diagram is an over-simplification of what occurs from level to level. The concept and trend holds true, the specifics about colors do not necessarily*

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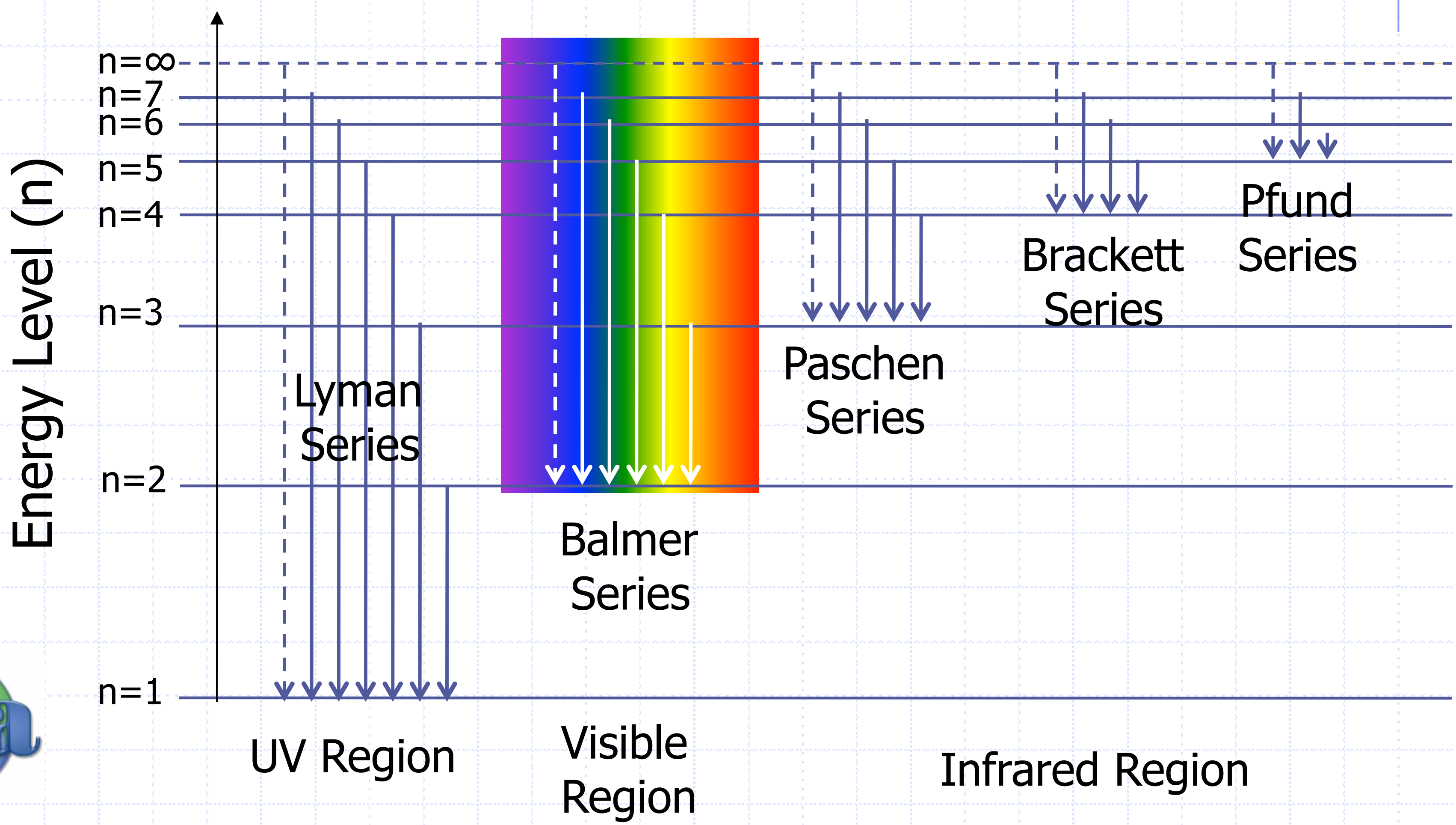
Hydrogen Emission

- The origin of each of hydrogen's emissions can be summarized through the following diagram



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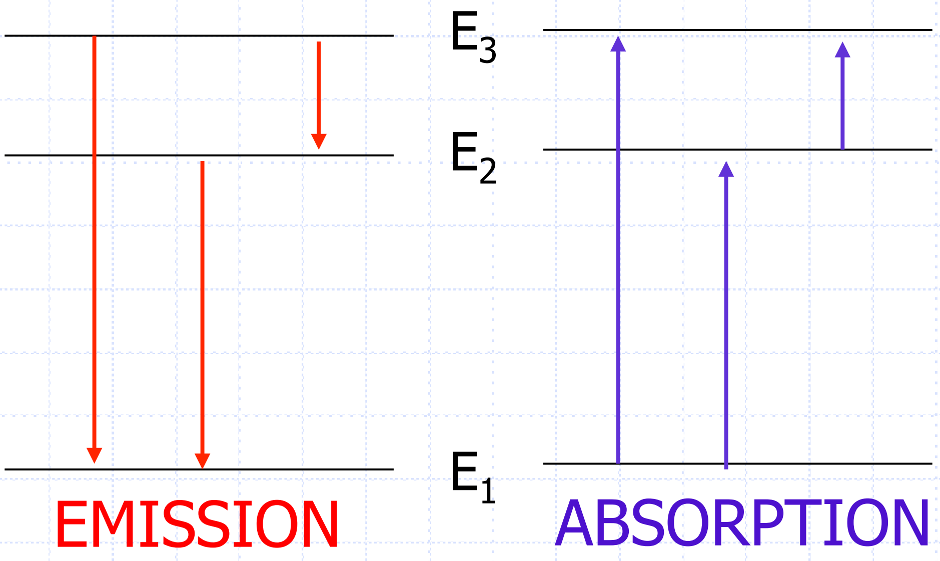
Absorption vs Emission

Distinguish between absorption and emission spectra and how each is produced

- **Emission Spectroscopy**
  - A molecule or atom undergoes a transition from a state of high energy (E_2) to low energy (E_1)
- **Absorption Spectroscopy**
  - A molecule or atom undergoes a transition from a state of low energy (E_1) to high energy (E_2)

The energy emitted or absorbed, which is the frequency (f) of the wave is given by the following relationship:

$$hf = \Delta E = E_2 - E_1$$



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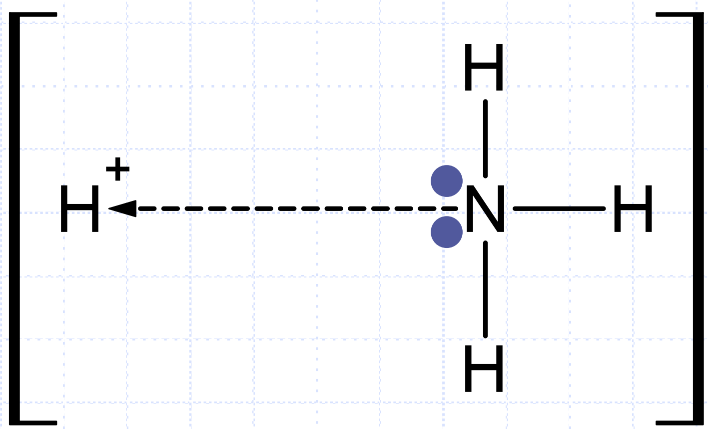
Coordinate Covalent Bonds

- When both electrons that are shared (in a single bond) come from the same atom, the bond is known as a **coordinate bond** or a **dative bond**.
  - Shown as an arrow (→) instead of a bond (-) where the electrons came from the source of the arrow
  - The **coordination number** is the number of bonds (to **ligands)** formed around the central atom
  - In Topic 08 (Acids and Bases) known as **Lewis acids and bases**



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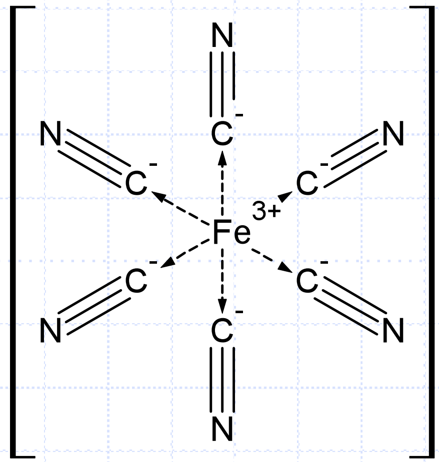
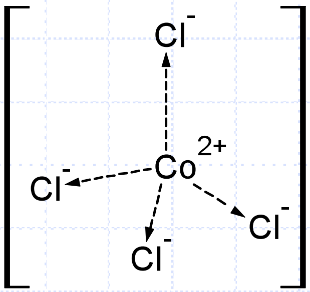
Formation of Complex Ion Compounds

Describe and explain the formation of complexes of d-block elements.

- The coordination number is simply the number of ligands attached to the ion:
  - $[Fe(CN)_6]^{3-}$ coordination of 6
  - $[Co(Cl)_4]^{2-}$ coordination of 4

Note: arrow are backwards





  - Each of the resultant complex ions will pick up a charged particle to form a neutral salt
    - If the ligand is charged, the species becomes more negative and must pick up another cation (metal)
    - If the ligand is neutral, the species remains positive and must pick up an anion (non-metal)

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Ligands and Splitting

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Describe the effect of different ligands on the splitting of the d orbitals in transition metal complexes

- Refer to topics 13&14 (HL Periodicity and Bonding) for further review on d-orbital splitting
- Transition metals form "complexes" in which coordinate covalent (dative) bonds are formed with nucleophilic ligands
  - Common Ligands
    - Halides, OH^-, H_2O, NH_3, CN^-, CO
    - Ex: $[Cu(H_2O)_6]^{2+}$, $[Cu(H_2O)_2(NH_3)_4]^{2+}$, $[Fe(CN)_6]^{3-}$
- Transition metals that are NOT colored
  - Zinc – completely full 3d subshell ($3d^{10}$)
  - Scandium – empty 3d subshell ($3d^0$)

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Ligands

Define the term ligand

- A d-block metal **complex-ion** consists of a d-block metal ion surrounded by a definite number of ligands.
  - **Ligands** are molecules or negative ions with lone pairs of electrons
  - Common ligands are: H_2O, NH_3, Cl^-, OH^-, CN^-
    - Also known as nuclophiles as they are attracted to the positive charge of a nucleus (in this case the effective nuclear charge of a transition metal ion).
  - Ligands share their lone pair with the empty orbitals in the central d-block
    - The ligands behave as Lewis Bases (e^- pair donors – Topic 08/18)

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Electron Configuration of Neutral T-metals

El.	#	Noble Not.		3d					4s
Sc	21	[Ar]$3d^{1}4s^{2}$	[Ar]	↑					↑↓
Ti	22	[Ar]$3d^{2}4s^{2}$	[Ar]	↑	↑				↑↓
V	23	[Ar]$3d^{3}4s^{2}$	[Ar]	↑	↑	↑			↑↓
Cr	24	[Ar]$3d^{5}4s^{1}$	[Ar]	↑	↑	↑	↑	↑	↑
Mn	25	[Ar]$3d^{5}4s^{2}$	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	26	[Ar]$3d^{6}4s^{2}$	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	27	[Ar]$3d^{7}4s^{2}$	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	28	[Ar]$3d^{8}4s^{2}$	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	29	[Ar]$3d^{10}4s^{1}$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	30	[Ar]$3d^{10}4s^{2}$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

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Electron Configuration of **Charged** T-metals

El.	#	Noble Not.		3d					4s
Sc^{3+}	21	[Ar]	[Ar]						
Ti^{2+}	22	[Ar]	[Ar]	↑	↑				
V^{2+}	23	[Ar]$3d^3$	[Ar]	↑	↑	↑			
Cr^{3+}	24	[Ar]$3d^3$	[Ar]	↑	↑	↑			
Mn^{2+}	25	[Ar]$3d^5$	[Ar]	↑	↑	↑	↑	↑	
Fe^{2+}	26	[Ar]$3d^6$	[Ar]	↑↓	↑	↑	↑	↑	
Co^{2+}	27	[Ar]$3d^7$	[Ar]	↑↓	↑↓	↑	↑	↑	
Ni^{2+}	28	[Ar]$3d^8$	[Ar]	↑↓	↑↓	↑↓	↑	↑	
Cu^{2+}	29	[Ar]$3d^9$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	
Zn^{2+}	30	[Ar]$3d^{10}$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	

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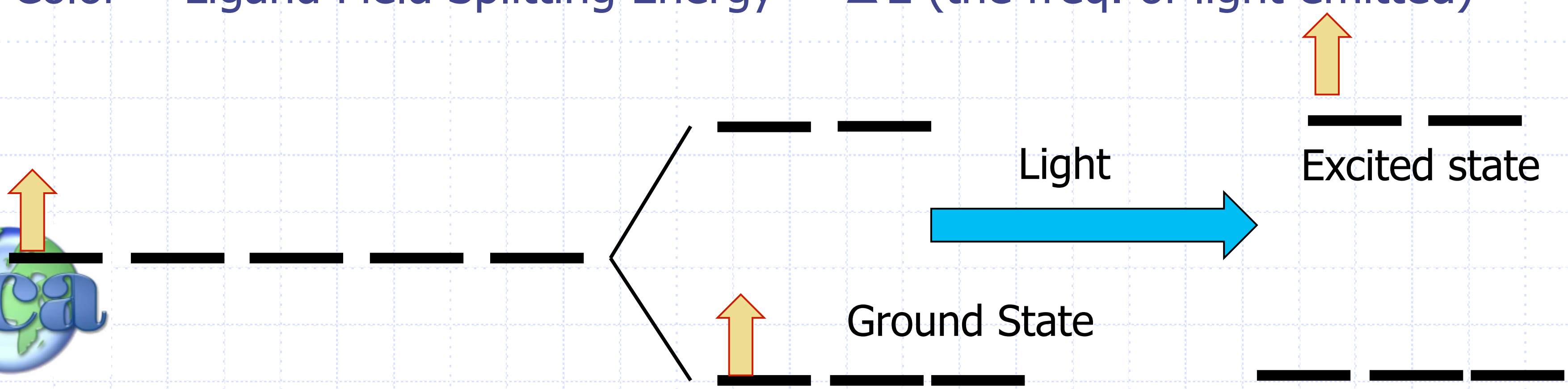
Colored Compounds

Explain why some complexes of d-block elements are colored

- Most d-block metal compounds are colored, both in solution and in the solid state.
- The colors are due to the presence of incompletely filled 3d sub-shells
- In an isolated gaseous d-block metal, the five 3d subshells are of equal energy and different orientations
- In a complex ion, the 3d sub-shells are oriented relative to the ligands – those close to the ligand experience repulsion and are raised in energy
- This 3d sub-shell is split into two energy levels
- Color = Ligand Field Splitting Energy = ΔE (the freq. of light emitted)



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Color and Transition Metals

Describe the factors that affect the color of transition metal complexes

- Factors that affect the Ligand Field Splitting Energy (color)
  - The transition metal charge and electron configuration
  - Nature of the ligand
  - Coordination number of the ligand
- For example

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(H_2O)_2(NH_3)_4]^{2+}(aq) + 4H_2O\,(aq)$$

pale blue — deep royal-blue

  - Changing the ligands, slightly modified the color as it changed the energy difference of the ligand field splitting

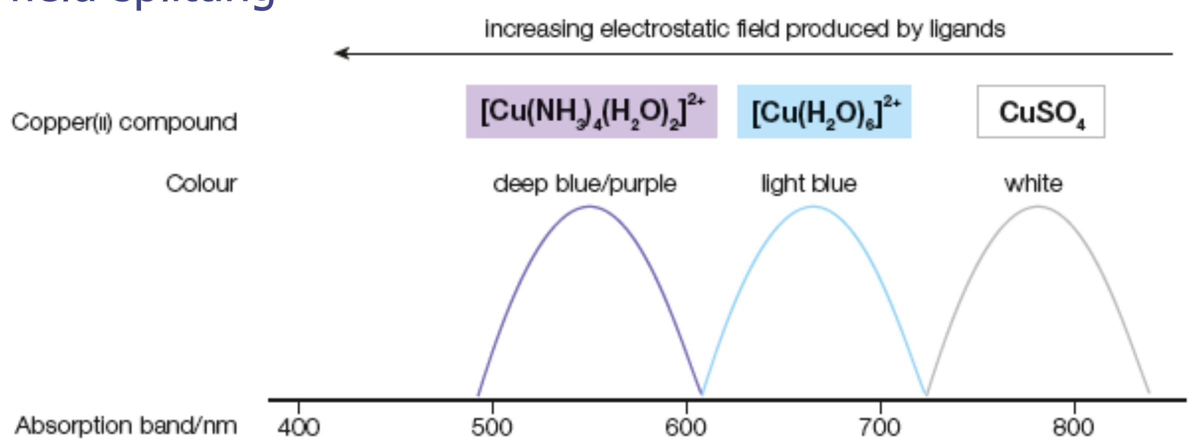

Figure 21.98 Absorption spectra and colours of selected copper(II) compounds showing the effect of a stronger ligand field

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Relative Splitting Energies

- Orbital Splitting Power:
  - $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$

- $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O$

  Blue　　　　　　　　　　　　　　Green/Yellow
  - Energy: Blue>Green/Yellow
  - Ligand Field Splitting: Decreased
    - Ligand: Cl^- causes weaker splitting than H_2O
    - Coordination: Less ligands (4 vs 6) causing repulsions

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Topic Justification

State the reasons for using analytical techniques

- **Qualitative Analysis**
  - The identification of elements or compounds present in a sample
  - Ex: Flame tests, precipitation reactions
- **Quantitative Analysis**
  - The determination of the amounts of elements or compounds present in a sample
  - Quality Control: Used to ensure that levels of contaminants or harmful residues are below specific levels
  - Structural Analysis: Identifying functional groups and structure of a molecule
  - Ex: Titrations, UV/Visible/IR Spectroscopy, chromatography

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Areas that utilize Analytical Techniques

- **Monitoring and Control of Pollutants**:
  - Presence of hazardous materials
    - Heavy Metals, Organic chemicals, Atmospheric pollutants
- **Clinical and biological studies**:
  - Levels of important nutrients in food
  - Body fluids (Iron, Cholesterol, etc)
- **Geological Studies**
  - For mining of minerals, metals, and metal complexes
- **Drug Discovery**
  - Confirmation of newly synthesized materials
- **Food Purity**
  - For pollutants, toxins, pathogens
  - To ensure that legal levels of additives are not exceeded